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Perfluoroalkyl Acid Uptake in Lettuce (Lactuca sativa) and Strawberry (Fragaria ananassa) Irrigated with Reclaimed Water

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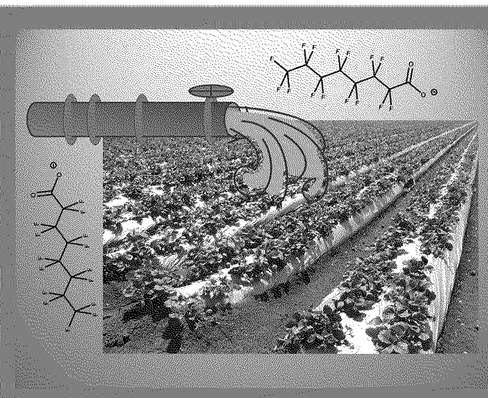
* Supporting Information



Using reclaimed water to irrigate food crops presents an exposure pathway for persistent organic contaminants such as perfluoroalkyl acids (PFAAs) to enter the human food chain. This greenhouse study used reclaimed water augmented with varying concentrations (0.2−40 μg/L) of PFAAs, including perfluorocarboxylates ($C_3F_7COO^-$ to $C_8F_{17}COO^-$) and perfluorosulfonates ($C_4F_9SO_2O^-$, $C_6F_{13}SO_2O^-$, $C_8F_{17}SO_2O^-$), to investigate potential uptake and concentration−response trends in lettuce (Lactuca sativa) and strawberry (Fragaria ananassa). In addition, studies were conducted to evaluate the role of soil organic carbon concentrations on plant uptake of PFAAs. PFAA concentrations in lettuce leaves and strawberry fruit were measured for each aqueous PFAA concentration applied. PFAA plant concentrations increased linearly with the aqueous concentration for all PFAAs, with PFCAs bioaccumulating to a greater degree than PFSAs in the edible portions of the tested plants. Chain-length-dependency trends were evident in both lettuce shoot and strawberry fruit, with decreasing concentrations associated with increasing chain length. Perfluorobutanoate (PFBA) and perfluoropentanoate (PFPeA), both short-chain PFAAs (<8 carbon chain length), accumulated the most compared with other PFAAs tested in the edible parts of both lettuce and strawberry. PFAA concentrations in strawberry root and shoot were also measured at selected PFAA aqueous concentrations (0.4, 4, and 40 μg/L). Short-chain perfluorocarboxylates were the dominant fraction in the strawberry fruit and shoot compartments, whereas a more even distribution of all PFAAs appeared in the root compartment. Lettuce grown in soils with varying organic carbon contents (0.4%, 2%, 6%) was used to assess the impact of organic carbon sorption on PFAA bioaccumulation. The lettuce grown in soil with the 6% organic carbon content had the lowest bioaccumulation of PFAAs. Bioaccumulation factors for lettuce were correlated to carbon chain length of PFAAs, showing approximately a 0.4 to 0.6 log decrease per CF_2 group. This study confirms that PFAAs can enter and bioaccumulate in food crops irrigated with reclaimed water. Bioaccumulation potential depends on analyte functional group and chain length, concentration in the reclaimed water, and organic carbon content of the soil.

INTRODUCTION

Perfluoroalkyl acids (PFAAs) are ubiquitous synthetic chemicals that are widely used in both consumer and industrial settings, and have attracted much attention with regard to their persistent, accumulative, and toxic nature.[1,2] The extensive use of PFAAs in consumer products means that municipal wastewaters are a collection vehicle for the compounds. In addition, the prominence of PFAAs in some manufacturing processes can lead to high levels in industrial wastewaters that also flow to wastewater treatment plants (WWTPs).[3] Most conventional WWTPs are ineffective at removing PFAAs[3,4] and, thus, may represent significant sources of PFAA releases into the environment.[5] Unlike many organic contaminants, the dual hydrophobic/lipophobic nature of PFAAs enables these compounds to reside in significant quantities in both the aqueous and sludge effluent streams of WWTPs.[4,6]

The aqueous effluent stream of a WWTP is, in general, returned to the surrounding aquatic environment; however, growing water scarcity is driving alternative uses of treated wastewater. In particular, interest in the use of recycled or reclaimed water, which typically consists of municipal wastewater (treated to remove pathogens, organic matter, and nutrients), for agricultural purposes is growing and is likely to continue in the future.[7] Reclaimed water has been safely used for many years in the U.S. for the irrigation of nonfood crops[8] and, on a more limited scale, for food crops eaten raw (e.g., in the Salinas Valley, CA). Recently, however, concerns have been

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raised regarding the presence of chemicals of emerging concern in reclaimed water.[9]

Although the U.S. Environmental Protection Agency has published guidelines for water reuse, no federal regulations govern water reclamation and reuse in the U.S., and thus, regulations or guidelines have been developed at the state level.[8] This nonunified approach has resulted in differing standards among states that have developed reuse criteria. Existing water reuse regulations for food crop irrigation in each state vary according to crop type and irrigation method, but are principally directed at health protection from microbial pathogens and do not typically include requirements addressing organic contaminants.[10]

The potential risks associated with bioaccumulation of organic contaminants are most easily studied in edible crops eaten raw since processing and cooking can add confounding factors, such as chemical transformation, chemical volatilization, or additional contamination by cookware or packaging.[11] Unfortunately, although data on the occurrence of many contaminants in reclaimed water are plentiful,[12−14] limited data exist on the potential for uptake of PFAAs from reclaimed water into edible plants. To date, human health risk assessments are generally based on plant uptake models primarily developed for neutral organic chemicals and are limited to crop-specific data.[15,16] PFAAs exhibit surfactant behavior, and thus, octanol−water partitioning coefficients used in traditional bioaccumulation modeling are not applicable to this class of compounds; instead, PFAA chain length is a better proxy for hydrophobicity.[17]

A few studies have demonstrated the potential for crop uptake of pharmaceuticals applied via real or simulated wastewater;[18−21] however, the behavior of the contaminants studied is very different from that of PFAAs, particularly in regard to charge. Felizeter et al.[22] reported uptake of PFAAs in lettuce plants via hydroponic solution, with higher concentrations of the short-chain (<8 carbon chain length) PFAAs accumulating in the leaves. However, fundamental differences between hydroponic and solid media experiments as well as differences in water quality between nutrient solutions and actual reclaimed water prevent direct applicability of these data to crops irrigated with reclaimed water and grown in soil. Blaine et al.[23] examined lettuce uptake of PFAAs from biosolids-amended soils and also found preferential short-chain accumulation in the lettuce leaves. However, as the bioavailability of PFAAs for uptake may vary considerably depending on the uptake matrix, these data may have limited applicability to crop uptake of PFAAs via reclaimed water.

This study was conducted to examine the uptake of PFAAs in lettuce (*Lactuca sativa* 'Multy') and strawberry (*Fragaria ananassa* 'Albion') via reclaimed water under conditions representative of current agricultural practices. Experiments were carried out using reclaimed water augmented with varying concentrations of PFAAs. The intent of this research was to elucidate PFAA accumulation potential in response to varying concentrations of PFAAs in reclaimed irrigation water. Lettuce and strawberry crops were chosen to represent typical food crops grown in the U.S. using reclaimed water. In addition, lettuce grown in soils with varying organic carbon (OC) content was used to assess the impact of OC sorption on PFAA bioaccumulation given the propensity of PFAAs to sorb to OC.[17]

MATERIALS AND METHODS

Chemicals. All calibration standards and stable isotopes were acquired from Wellington Laboratories (Guelph, ON, Canada) and prepared using established protocols.[23] Specific PFAAs used in this study include perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and perfluorooctanesulfonate (PFOS); PFAAs and corresponding surrogate standards are listed in Table S1. Spiking solutions for dosing experiments were prepared from individual standards purchased from Sigma-Aldrich (St. Louis, MO). High purity Chromasolv dichloromethane, HPLC-grade methanol, and all other reagent grade solvents were acquired through Sigma-Aldrich. Water for extractions was obtained from a Milli-Q system (Millipore, Billerica, MA), whereas HPLC-grade water was utilized for liquid chromatography tandem mass spectrometry (LC−MS/MS) analysis. Extraction cleanup was facilitated with Chromabond diamino from Macherey-Nagel Inc. (Bethlehem, PA) and Supelclean ENVI-Carb from Sigma-Aldrich.

Greenhouse Study. Plant uptake experiments were conducted in a climate controlled greenhouse with two food crops, leaf lettuce (*L. sativa* 'Multy') and strawberry (*F. ananassa* 'Albion'). These selected cultivars are similar to cultivars currently grown in the western U.S. using reclaimed water. Five replicate plants were grown for each set of experimental conditions. Pots (15 cm diameter) were randomly arranged to account for any spatial variations in light and temperature within the greenhouse. Day temperatures ranged from 18 to 21 °C, and night temperatures ranged from 10 to 13 °C. Full spectrum, metal halide and high pressure sodium supplemental lighting (Plantmax 1000W bulbs) was also supplied to achieve 16 h of daylight to mimic field conditions. Additional information regarding plant propagation and cultivation can be found in the Supporting Information (SI).

Reclaimed water was supplied by the Mines Park pilot-scale Sequencing Batch/Membrane Bioreactor. This test site at the Colorado School of Mines treats raw sewage from a student apartment complex (a graduate housing community of ~400 individuals); a full description of the site can be found elsewhere.[24] Although the effluent from Mines Park was not specifically tailored to meet the reclaimed water regulations of any particular region, the water represented a steady and realistic source of reclaimed water for the experiments (SI Table S3). Concentration-dependent accumulation was examined by spiking the reclaimed water with eight levels of PFAAs (0.2, 0.4, 1, 2, 4, 10, 20, 40 μg/L) in addition to using ambient reclaimed water and tap water (control). This concentration range was chosen to give a range of values starting with ambient concentrations found in the Mines Park reclaimed water (~0.02 μg/L), bracketing typical WWTP effluent concentrations (0.2−4 μg/L),[5] and reaching concentrations representative of contaminated groundwater (10−40 μg/L).[25,26] To assess the accuracy of the actual irrigation solutions as opposed to the nominal concentrations, aliquots from each solution were analyzed. The lowest recoveries were for PFNA (36%) and PFOS (23%), the strongest sorbing analytes, most likely as a result of losses onto the walls of the watering containers. The linearity of the aqueous concentrations remained fairly constant for each analyte, with each applied concentration being 1.5−3

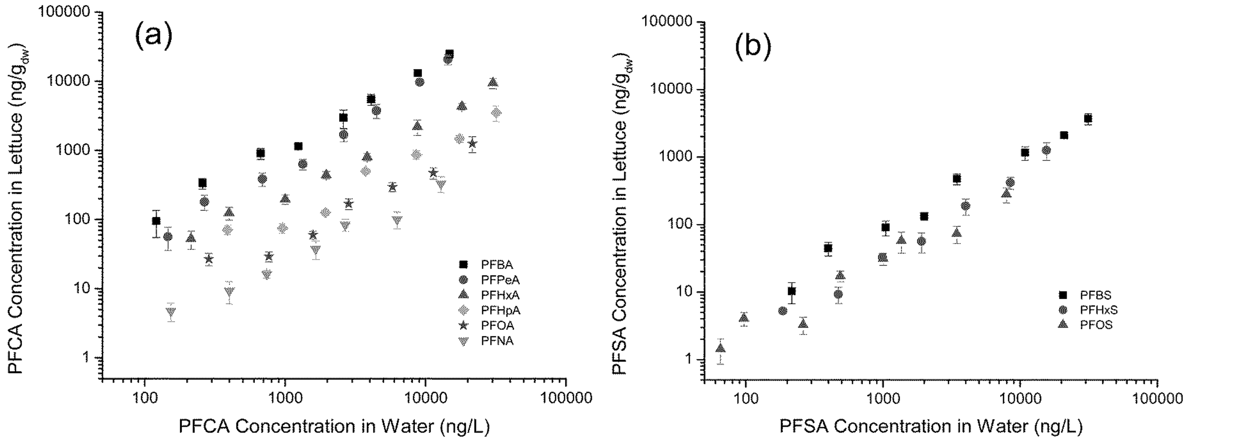

Figure 1. Concentrations of PFCAs (a) and PFSAs (b) in lettuce leaves versus measured aqueous concentration of PFAAs. Means and standard errors (n = 5) are shown.

times the next lowest concentration. Both the tap water control and ambient reclaimed water had trace detections (<25 ng/L) of PFHxA, PFOA, and PFOS. Measured concentrations of PFAAs (SI Table S2) were used in all calculations. Plants received PFAAs via hand watering three times a week, 100 mL of solution per lettuce plant and 200 mL of solution per strawberry plant. Additional information on the reclaimed water quality is found in SI Table S3.

Because soil organic matter can significantly impact the bioavailability of PFAAs,[27] a prepared sandy soil mix (3:1 sand/topsoil by mass) with only 0.4% OC was used to represent a "worst-case" scenario in terms of bioavailability. Plant essential nutrients were supplied by mixing a single application of slow release Osmocote (nitrogen−phosphorus−potassium: 19−6−12) into the media (~5 g/plant). To more specifically test the impacts of OC on PFAA uptake, lettuce was grown in two additional soils with varying OC content (2%, 6%) at a single PFAA concentration (10 μg/L). Details on the soils utilized are provided in the SI.

Edible portions of lettuce and strawberry plants were harvested at maturity. In addition, after sufficient strawberry fruit biomass was harvested, whole strawberry plants were collected and separated into root and shoot portions. All plant material was frozen (−20 °C) in PFAA-free plastic bags prior to analysis. Additional details concerning soil and produce sampling are found in the SI.

Sample Extraction and Data Analysis. Homogenized plant samples (0.5−2 g) were prepared and extracted using the protocol from Blaine et al.[23] Lettuce shoots from all experimental replicate pots (n = 3−5) were extracted independently, and concentrations were averaged. Ripe strawberry fruit from the replicate plants at each aqueous applied concentration were composited to achieve adequate biomass for extraction, resulting in composited averages of analytical triplicate measurements. Strawberry shoot and root experimental replicates for three aqueous concentrations (0.4, 4, 40 μg/L) were extracted separately to enable an estimation of interpot variability (since field replicates of fruit were composited); concentrations in replicate plants (n = 3−5) were averaged to obtain sample values. All results for plant concentrations are presented in terms of a dry weight basis. Aqueous sample analyses were completed per established methods.[28]

Samples were analyzed with isotope dilution using LC−MS/MS under conditions outlined in previous work.[23] Briefly, chromatography was performed using a Shimadzu LC-20AD unit (Kyoto, Japan) by injecting samples onto a Gemini C18 column with a 3-μm particle size (Phenomenex, Torrance, CA). In addition, two transitions for each PFAA were observed using an ABSCIEX 3200 (ABSCIEX, Ontario) with negative electrospray ionization operating in scheduled multiple reaction mode. Quantitation of LC−MS/MS data was accomplished using Analyst software.

Quality Assurance and Control. All of the strawberry fruit, as well as approximately 20% of all other samples, were extracted and analyzed in triplicate. The relative standard deviation for all analytical replicates averaged <25%. One laboratory blank with surrogate standard and one double blank without surrogate standard were prepared for each batch of samples. Limits of quantitation (LOQ) for plant material ranged from 0.07 to 29 ng/g; LOQs were determined by the lowest calibration standard calculated to be within 30% of its actual value and were analyte-, matrix-, and run-dependent. LOQs were also required to be at least twice as high as the highest concentration in the corresponding blanks and have signal-to-noise ratios >30. If a minimum of three pot replicates were above the LOQ, an average value was calculated for that treatment; otherwise, the value was reported as <LOQ. To account for any losses during the extraction process, an internal surrogate standard was employed for each analyte. In line with previous work analyzing PFAAs in plant tissues,[29] surrogate recovery for the samples averaged 43% for root tissues, 33% for shoot tissues, and 45% for fruit tissues across all analytes. Statistical analysis including all calculations of regression equations was completed using OriginPro 9.0.

Bioaccumulation Metrics. Bioaccumulation factors (BAFs) for lettuce leaves (at the 10 μg/L applied concentration) and, more specifically, fruit-to-soil concentration factors[29] (FCFs) for strawberry fruit (at the 0.4, 10, and 40 μg/L applied concentrations) were calculated for each PFAA that had concentrations in the plant tissues above the LOQ. To enable comparisons to previous studies examining PFAA bioaccumulation from soils, the aqueous concentration (C_w) was first converted to an estimated soil concentration (C_s) using the respective solid−water partitioning coefficient (K_d) for each soil and analyte (eq 1).

$$C_s\left(\frac{ng}{kg}\right) = C_w\left(\frac{ng}{L}\right) \times K_d\left(\frac{L}{kg}\right) \quad (1)$$

Although it remains unclear as to whether equilibrium conditions were present, measured single point K_d values were used in the absence of soil pore water concentrations; moreover, previously measured isotherms for PFAAs were fairly linear (Freundlich n values ~ 0.9−1) providing validity for this estimation method.[17] More information concerning the determination of K_d values can be found in the SI. Concentration factors were then calculated as in previous work[23,29] by dividing the concentration of chemical in the respective plant tissue on a dry weight basis by the concentration of chemical in the soil. In addition, intercompartmental concentration factors (fruit to shoot and shoot to root) were calculated as in previous work[29] for strawberry plants grown at the 0.4, 4, and 40 μg/L applied concentrations.

RESULTS AND DISCUSSION

Concentration-Dependency Trends. All PFAAs measured in lettuce leaves showed predominately linear concentration−response relationships (Figure 1), suggesting passive transport through the plant.[30] The slopes of the nonlog linear regressions for each analyte (SI Figure S1) imply preferential uptake by the short-chain PFAAs. In general, PFCAs accumulated in much greater quantities than the perfluorosulfonates (PFSAs) with concentrations in lettuce leaves receiving the highest application of PFAAs reaching 25 μg/g for PFBA. Conversely, PFCA accumulation was <LOQ in the lettuce treated with control tap water and ambient reclaimed water (SI Table S6).

Short-chain PFCA accumulation in strawberry fruit was also linear with increasing aqueous concentrations. Concentrations in fruit receiving the highest application of PFAAs were >10 μg/g for PFBA and PFPeA (SI Table S7). PFHxA accumulation in strawberry fruit was not measured above the LOQ except for the four highest aqueous doses. PFHpA, PFOA, and PFNA concentrations were all <LOQ. Linear concentration−response relationships, similar to those observed in lettuce, are shown in Figure 2, and the nonlog linear regressions are displayed in SI Figure S2. Of the PFSAs, only PFBS concentrations were above LOQ, and accumulation in the strawberry fruit was minimal (<56 ng/g) compared with the PFCAs (SI Table S7). The lack of PFSA accumulation in the fruit compartment is consistent with previous findings in tomato and pea fruit.[29] The observed bias against accumulation of long-chain PFAAs in the fruit compartment may suggest that other specific transport mechanisms exist for long-chain PFAAs. Wen et al.[31] studied uptake of PFOA and PFOS by maize and found indications of potential active transport for PFOA, partial aquaporin (water channel) transport for PFOS, and limited carrier-mediated transport through different anion channels for both analytes. Although strawberry plants are very different from maize, similar mechanisms may contribute to the lack of accumulation of long-chain PFAAs in strawberry fruit.

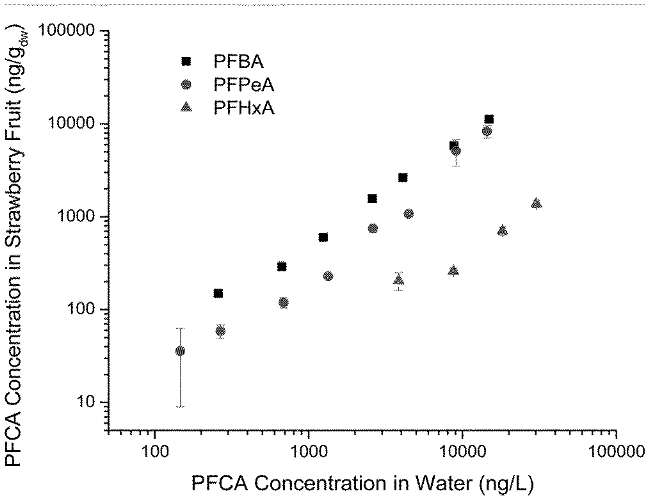

Figure 2. Concentrations of PFCAs in strawberry fruit versus measured aqueous concentration of PFAAs. Means of composited berries are shown with analytical standard deviation (n = 3).

Chain Length Trends. As evidenced in Figures 1 and 2, concentrations in both lettuce leaves and strawberry fruit decreased as PFAA chain length increased. To further illustrate this trend, PFAA concentrations for a single aqueous applied concentration (10 μg/L) in both lettuce and strawberry are provided in Figure 3. In lettuce leaves, PFAA concentrations spanned more than an order of magnitude from PFBA to PFNA, a gain of 5 carbons, and also more than an order of magnitude from PFBS to PFOS, a gain of 4 carbons. In strawberry fruit, PFAA concentrations spanned more than an order of magnitude from PFBA to PFHxA, a gain of only 2 carbons, further evidencing the disparity of accumulation potential between short- and long-chain PFCAs. This preferential accumulation of short chain carboxylates in plants is consistent with previous findings.[29]

Strawberry Plant Compartments. Nonedible portions of strawberry plants were analyzed to assess interpot variability (22%) and help elucidate bioaccumulation trends within the plant. At the highest aqueous concentration applied (40 μg/L), strawberry root concentrations were greatest for PFHxA (5450 ng/g; SI Table S8), strawberry shoot concentrations were greatest for PFBA (3900 ng/g; SI Table S8), and strawberry fruit concentrations were greatest for PFPeA (11,500 ng/g; SI Table S7). Moreover, the concentrations of both PFBA and PFPeA in the fruit were more than twice that of any analyte that accumulated in the root or shoot compartments. The distribution of PFAAs in each plant compartment (root, shoot, and fruit) for a representative aqueous concentration (4 μg/L) is shown in Figure 4. Of the three compartments in the strawberry plant, the root compartment had the greatest accumulation of PFAAs (2840 ng/g), and the distribution of PFAAs in the root compartment was fairly evenly spread, confirming the lack of selectivity of analytes in the root compartment described by Blaine et al.[29] The shoot compartment had the lowest total accumulation of PFAAs (705 ng/g) of the three compartments, and the accumulation was dominated by the short-chain analytes, PFBA, PFBS, and PFPeA. The fruit compartment had almost as much total accumulation (2520 ng/g) as the root compartment; however, the distribution of PFAAs was highly skewed toward the short-chain PFCAs, and no PFSAs were present in the fruit. Because plants were grown with limited irrigation (i.e., not hydroponically) to represent field conditions, a high percentage of the water taken up was most likely used for fruit development;[32,33] the relatively low amount of water transpired versus the water used for fruit development could explain the higher accumulation of PFAAs in the fruit versus the shoot.

The mass distribution between plant compartments for each analyte can be estimated by multiplying typical dry weights for

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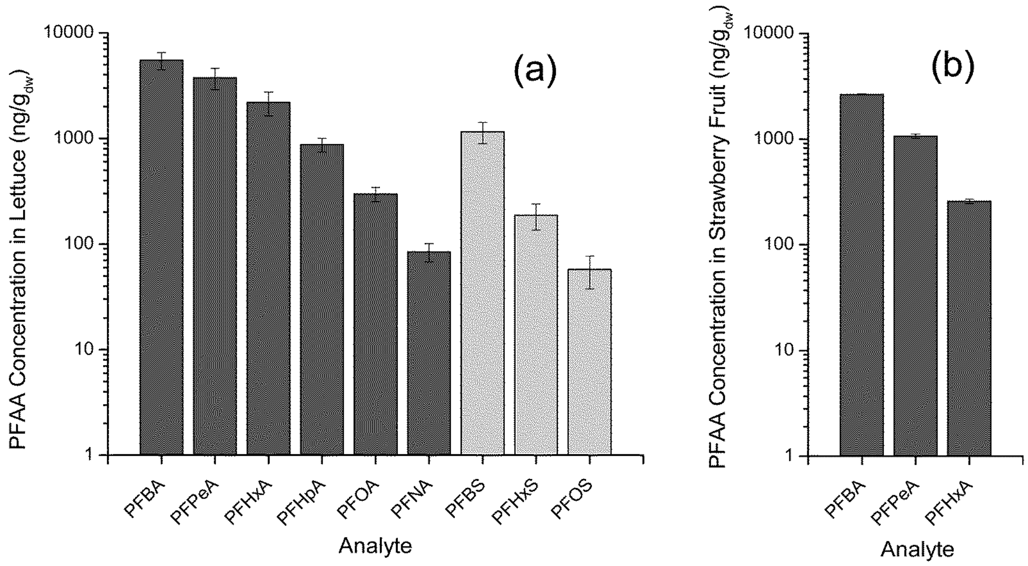

Figure 3. Concentrations of PFAAs in lettuce leaves (a) and strawberry fruit (b) for the aqueous applied PFAA concentration of 10 μg/L. Mean and standard error for lettuce (n = 5) are shown. Means of composited berries are shown with analytical standard deviation (n = 3).

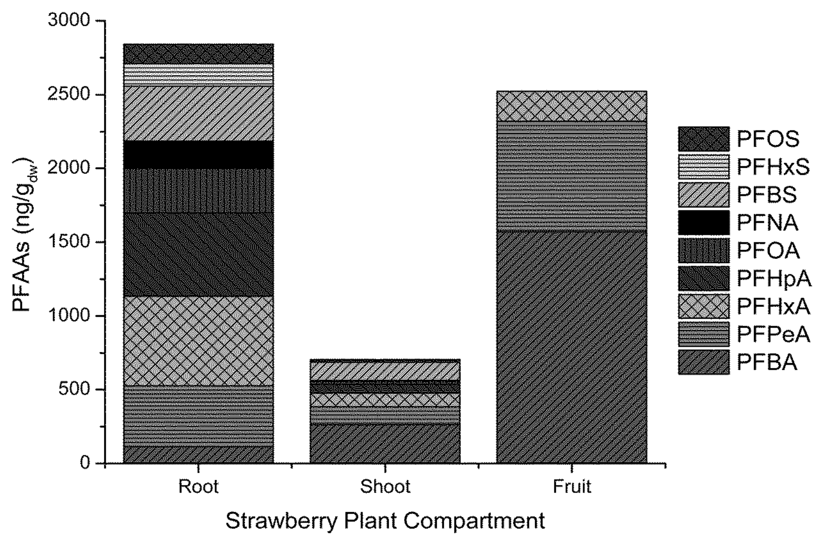

Figure 4. Distribution of PFAAs in strawberry root, shoot, and fruit compartments for the applied aqueous PFAA concentration of 4 μg/L.

each compartment (1.3 g for root, 4 g for shoot, 3 g for fruit) by the concentration of each analyte in the respective compartment. The dominant fractions (>65%) of PFBA and PFPeA resided in the fruit compartment, whereas the dominant fractions (>70%) of the long-chain PFAAs accumulated in the root compartment (SI Figure S3). Similar trends concerning mass distribution within plant compartments were observed for both lower (0.4 μg/L) and higher (40 μg/L) aqueous concentrations.

FCF values (converted to a soil basis for the 10 μg/L applied aqueous concentration) for strawberry ranged from the 200s for PFBA and PFPeA to 35 for PFHxA (SI Table S9). Although the data are limited, when plotted versus carbon chain length, the overall average decrease of FCF per CF_2 group was ~0.3 log units (Figure 5). These results are similar to the findings of Blaine et al.[29] for tomato and pea fruit, as shown alongside the strawberry fruit data in Figure 5. The differences in FCF values for strawberry as compared to tomato and pea could be due to differences in plant morphology or to the delivery of PFAAs via irrigation water versus biosolids. At the highest aqueous concentration (40 μg/L), the FCF versus chain length trend is also ~0.3 log units, indicating consistency in accumulation trends at varying concentrations (SI Figure S4). Intercompartmental factors for strawberry plotted versus PFAA chain length (SI Figure S5) showed a decrease of 0.2 log units from fruit to shoot per CF_2 group and 0.3 log units from shoot to root per CF_2 group. These factors also correspond well to the intercompartmental factors calculated for tomato and pea fruits from previous work[29] (SI Figure S5).

Lettuce–Soil Organic Carbon Study. To assess the impact of soil sorption on plant uptake of PFAAs, lettuce was grown in soils with differing OC contents and compared with the lettuce grown in the sand–soil mix. Lettuce grown in the two additional soil treatments (2% and 6% OC content) at the 10 μg/L applied concentration accumulated similar (in general within a factor of 3) PFAA concentrations to that grown in the sand–soil mix (SI Table S10). PFBA and PFPeA concentrations were highest for lettuce grown in all three soils.

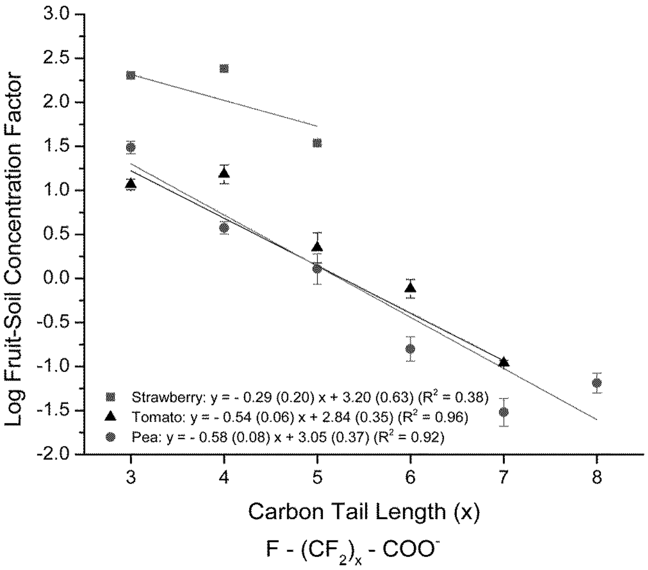

Figure 5. Correlations for PFCAs between log fruit−soil concentration factors and carbon chain length in strawberry, tomato, and pea. Strawberry values from this study were from the 10 μg/L applied aqueous concentration; tomato and pea values were from a previous study.[29] Means and standard errors are shown (n = 3 to 5). Linear regressions with slopes, intercepts, and associated error values are shown.

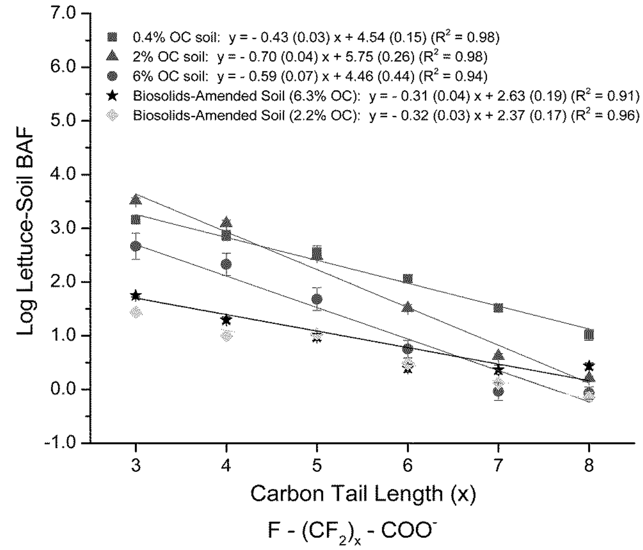

Figure 6. Correlations for PFCAs between log BAFs and carbon chain length in lettuce. Log BAFs from lettuce grown in soils with varying OC content (0.4%, 2%, 6%) at the 10 μg/L applied concentration are shown alongside values from lettuce grown in biosolids-amended soils in a previous study.[23] Means and standard errors are shown (n = 3−5). Linear regressions with slopes, intercepts, and associated error values are shown.

Concentrations ranged from approximately 15 μg/g of PFBA to 47 ng/g of PFNA in the 2% OC soil and from almost 5 μg/g of PFBA to 21 ng/g of PFNA in the 6% OC soil (SI Table S10).

Lettuce BAFs for all three soil treatments at the 10 μg/L applied concentration varied widely, spanning more than 2 orders of magnitude within each treatment. The lettuce grown in the 6% OC soil had the smallest BAF values for all PFAAs, presumably because of the sorption in the media (SI Table S11). All BAFs, with the exception of PFNA and PFOS in the 6% OC soil, were >1, indicating the accumulation of PFAAs in the lettuce. PFNA and PFOS have the highest K_d values of the PFAAs in this study (SI Table S4), so it follows well that they would exhibit minimal bioavailability in the highest OC content soil.

A linear relationship between log BAF values and carbon chain length is shown in Figure 6 for lettuce grown in each soil treatment. For each increase in carbon chain length, the BAF decreased ~0.4−0.7 log units. In addition, lettuce grown in two different PFAA contaminated biosolids-amended soils (2.2% and 6.3% OC) from a previous study[23] are plotted alongside the values from the present study for comparison. The slopes of all lines are somewhat similar (−0.31 to −0.70), with the slopes of biosolids-grown lettuce being slightly flatter than the lettuce grown with aqueous-applied PFAAs. This difference could indicate that the mobility of the PFAAs supplied by aqueous application allows immediate plant uptake prior to significant sorption in the soil. Figure 6 assumes that the irrigation solution is representative of pore water and that the water−soil system had reached equilibrium prior to plant uptake. In reality, however, equilibrium may not have been reached, thus increasing the bioavailability of the PFAAs applied in the reclaimed water. The lettuce slopes from the present study represented in Figure 6 may therefore be artificially steep compared with equilibrium conditions; however, they may be more representative of actual field conditions. Regardless, greater bioaccumulation overall is seen in the lettuce plants from the present study, suggesting that the mobility and bioavailability of PFAAs is greater when delivered via irrigation water as compared with biosolids-amended soil.

Implications. The results of this study are novel and important because it is the first of its kind to examine PFAA accumulation in food crops simulating, at least in part, a real-world field scenario by using authentic reclaimed water as the delivery medium. Certainly, real-world conditions such as the dilution of the contaminant concentrations crops are exposed to as a result of precipitation, perennial application of reclaimed water (potentially leading to a higher exposure concentration due to contaminant accumulation in the soil), and other numerous water management factors further complicate the picture for real-world extrapolation. Regardless, the data presented herein show clearly that PFAAs can be taken up and accumulated into food crops grown in soil and irrigated with reclaimed water, suggesting the potential for human exposure if irrigation water contains PFAAs. At typical WWTP effluent concentrations of PFAAs (0.02−4 μg/L),[5] values reached up to 0.2 μg/g for PFOA and 3 μg/g for PFBA in lettuce and up to 2 μg/g for PFBA in strawberry fruit. In addition, at higher aqueous concentrations, more representative of contaminated surface or ground waters (10−40 μg/L),[25] concentrations of PFAAs accumulated up to 1 μg/g for PFOA and 25 μg/g for PFBA in lettuce and up to and 11 μg/g for PFBA in strawberry fruit. The proposed subchronic reference dose for PFOA according to the U.S. EPA is 0.2 μg/kg-day;[34] for an average 70 kg adult, the maximum daily allowance of PFOA would then be 14 μg/day. If a person were to consume lettuce irrigated with contaminated water (40 μg/L of PFOA, well above the provisional health advisory level for drinking water of 0.4 μg/L[35]), then presumably, less than half of a small head of lettuce (126 g on a wet weight basis) would be enough to reach the daily maximum for PFOA. Concentrations of short-chain PFAAs in the lettuce would be even higher;

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however, substantial toxicological data are lacking for short-chain PFAAs. Although the levels of PFAAs in lettuce and strawberries irrigated with typical WWTP effluent would be expected to be considerably lower, concerns may arise if the WWTP received significant inputs from fluorochemical-using industries.

The concentration-dependent response for all PFAAs in lettuce and for short-chain PFAAs in strawberry fruit implies that PFAA accumulation in this range of aqueous concentrations does not plateau, and thus, the uptake potential for crops grown with highly contaminated water (e.g., surface water or groundwater near industry) is great. Long-chain PFCAs and PFSAs, however, do not readily accumulate in high quantities in strawberry fruit, regardless of increased aqueous concentration, and therefore, indications are that fruit may not be a major route of exposure for long-chain PFAAs. In general, bioaccumulation patterns observed in this study are consistent with literature[22,23] showing greater uptake and accumulation for PFCAs over PFSAs and for short-chain PFAAs over long-chain PFAAs. These plant compartment accumulation trends are important with respect to assessing potential human exposure through food crop consumption. As industry trends shift toward the manufacture of short-chain PFAAs, increased concentrations of shorter PFAAs in WWTP effluents can be expected.

If the current use of reclaimed water for food crops is to be sustained or increased, concerns about the potential contamination of food products must be fully addressed through careful scientific study, evaluation, and communication with the public. Future research is warranted by this potential exposure route to humans. More work is needed to understand PFAA transport mechanisms in additional crops. Investigations of crop uptake using a broader suite of PFAAs present in reclaimed water, including potential precursors of PFAAs, are also needed to expand the body of knowledge on this emerging topic of concern.

ASSOCIATED CONTENT

* Supporting Information

Additional details are available regarding PFAA standards, reclaimed water quality, soil characteristics, greenhouse experiment details, PFAA concentrations in lettuce (shoots) and strawberry (fruits, shoots, and roots), linear regressions for concentration-dependency study, mass distribution of PFAAs in plant compartments, plots of strawberry intercompartmental factors versus carbon chain length, and lettuce concentration and BAF values for organic carbon study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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